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Electrical investigation of the interface band structure in rubrene single-crystal/nickel junction

Yuta Kitamura,¹ Eiji Shikoh,¹ Satria Zulkarnaen Bisri,^{2,3} Taishi Takenobu,^{3,4} and Masashi Shiraishi^{1,4,a)}

¹Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560-8531, Japan

²Department of Physics, Graduate School of Science, Tohoku University, Sendai 980-8577, Japan

³Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan

⁴PRESTO, Japan Science and Technology Agency (JST), Saitama 332-0012, Japan

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The electronic structure of the interface between rubrene ($C_{42}H_{28}$) single crystal and ferromagnetic Ni is studied using an electrical method from a viewpoint of spintronics applications of organic single crystals. The Schottky barrier height at the interface is estimated to be 0.56 eV, and our finding is compared with previous results in spectroscopic method. This study clarifies the importance of electrical investigations of the Schottky barriers for various ferromagnet/organic systems and suggests that functionalization and carrier doping to rubrene single crystals are potential for obtaining the thinner barriers and yielding conclusive electrical spin injection. © 2011 American Institute of Physics. [doi:10.1063/1.3615704]

Organic spintronics^{1,2} has attracted significant attention as a means of utilizing a functionality of a spin degree of freedom to molecular electronics, because organic molecules comprise light elements such as carbon and hydrogen, thus the spin orbit interaction in organic molecules is smaller than in inorganic materials. Therefore, spin carriers in organic molecules can be hardly scattered, resulting in longer spin relaxation times and length. Spin relaxation length also becomes longer when carrier mobility in semiconducting molecules is larger, and thus semiconducting organic single crystal (OSC), which exhibits a large mobility, is suitable for spin transport. Rubrene single crystal is currently regarded as the best semiconductive OSC, since band conduction was realized^{3,4} and the mobility is the largest among all of OSCs.⁵ Hence, functional devices made from semiconductive OSCs, such as spin transistors, can be realized, provided that spin injection into the OSC is achieved.

One of the current obstacles is to realize spin injection into OSCs results a formation of an interfacial Schottky barrier between electrodes and OSCs, which is often induced by an electric double layer. In this sense, a characterization of the interface between electrodes and OSCs is strongly demanded, and several studies using x-ray and ultraviolet photoemission spectroscopy (XPS and UPS) techniques has been conducted in Co/pentacene thin film/Co and Co/Alq₃ thin film.^{6,7} However, a study for OSCs and ferromagnetic electrodes for organic spintronics applications has not been fully conducted yet.⁸ The purpose of this study is to focus on an interface electronic structure between a rubrene single crystal and ferromagnet. We have chosen Ni as a ferromagnetic electrode, because Ni possesses comparatively large work function compared with the other ferromagnetic metals (Fe, Co...),⁹ which is thought to be suitable for hole injection to rubrene single crystals.

The rubrene single crystal was grown by means of a physical vapor transport technique.¹⁰ The rubrene single

crystal thus formed was transferred into a glove box without exposure to air in order to avoid oxygen adsorption. The crystals were laminated on a glass substrate by a flip crystal technique.¹¹ Au, with 45 nm thickness, was evaporated by vacuum thermal evaporation using a shadow mask. The Ni electrode was also evaporated by a same method and the thickness of the Ni was also set to be 45 nm. It was reported that the contact resistance of a rubrene single crystal on Ni was smaller than that on Au under the presence of NiO_x.⁸ NiO_x is anti-ferromagnet, which impedes spin injection. Note that we have conducted the evaporation of the Ni electrodes in the evaporation chamber that is directly connected with the glove box, which enables us to avoid an oxidation in the Ni/rubrene interface. Figure 1 shows that the device possesses a lateral Au/rubrene single-crystal/Ni structure equipped with a top electrode configuration. The current-voltage characteristics were measured using a sub-femtoampere remote source meter (Keithley 6430) in a vacuum probe system equipped with a temperature controller (Scientific Instrument Model 9700). The temperature of the samples was controlled in the range of 270–350 K in 10 K intervals. Work function of Au and Ni, and an ionization potential of rubrene single crystal were measured by photoemission spectroscopy in atmosphere (Riken Keiki, AC-2).

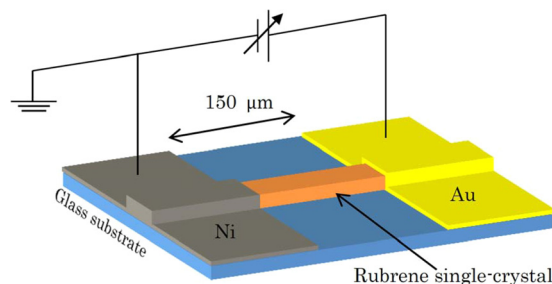


FIG. 1. (Color online) Schematic representation of a rubrene single-crystal device.

^{a)}Electronic mail: shiraishi@ee.es.osaka-u.ac.jp.

Figure 2(a) plots the current-voltage (I - V) characteristics of the Ni/rubrene single-crystal/Au junction at 300 K, wherein typical diode characteristics can be observed and no hysteresis was observed in the I - V curve. The electric current was detected when charged carriers were injected from the Au, not from the Ni. It is noted that because the work functions of the Au and the ionization potential of the rubrene were measured to be 5.41 ± 0.06 eV and 5.05 ± 0.08 eV, respectively, the contact between Au and rubrene single crystal is expected to be Ohmic when carrier are injected from the Au to the rubrene. Furthermore, the similar Ohmic behavior in electric measurements was also observed in our previous study,¹² where the same sample fabrication method using the glove box and the evaporation chamber without oxygen exposure of samples was introduced. Thus, these observations corroborates that the contact between the Au and the rubrene in this device is Ohmic-like. The I - V characteristics obtained were fitted using the following equation based on the thermionic emission theory by Bethe,¹³

$$I = I_0 \left(\exp \left(\frac{eV - IR_s}{nkT} \right) - 1 \right) + I_g, \quad (1)$$

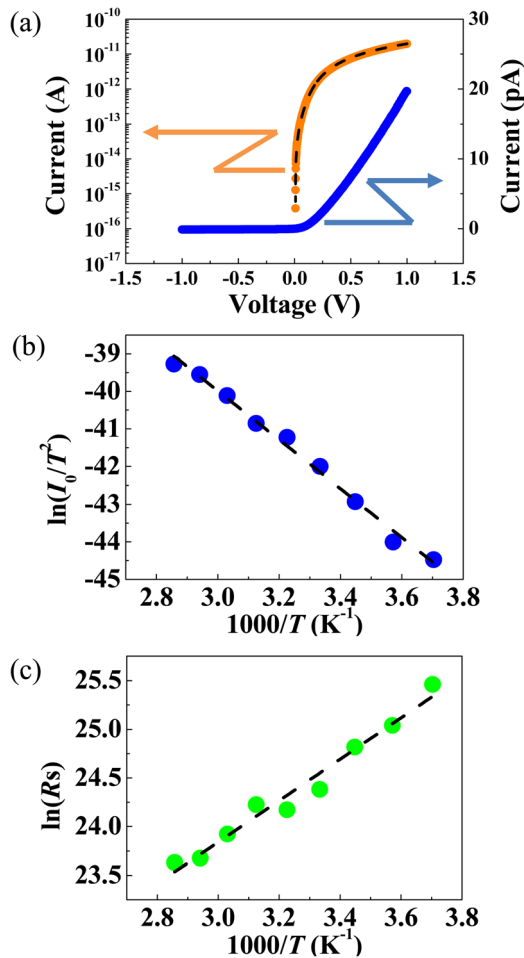


FIG. 2. (Color online) (a) Semi-log and linear plots show the current-voltage characteristics of a rubrene single-crystal Schottky diode at 300 K. The dashed line is the fitting curve obtained using the thermionic emission model. (b) Temperature dependence of $\ln(I_0/T^2)$ (symbols) and the fitted plot (dashed line). (c) Temperature dependence of $\ln(R_s)$ (symbols) and the fitted line (dashed line).

where I_0 , e , V , I , R_s , k , n , T are the inverse saturation current, the elementary charge, the applied voltage, the measured current, the series resistance of the device, the Boltzmann constant, the ideality factor, the temperature, and the background current, respectively. The inverse saturation current in the thermionic-emission theory is expressed as

$$I_0 = A^* T^2 \exp \left(- \frac{e\Phi_B}{kT} \right), \quad (2)$$

and therefore, Eq. (2) can be rewritten as

$$\ln \left(\frac{I_0}{T^2} \right) = \ln A^* - \frac{e\Phi_B}{kT}, \quad (3)$$

where A^* is the Richardson constant and Φ_B is the Schottky barrier height. By implementing the fitting using Eq. (1), n , R_s , and I_0 were estimated to be 1.52, 38.8 G Ω , and 51.8 fA, respectively. Even when the temperature was varied, the well-fitting was carried out and the n -values were estimated to be 1.49 ± 0.54 , indicating that this device was a good diode.¹² Figure 2(b) shows the variant of $\ln(I_0/T^2)$ versus $1000/T$. From the fitting using Eq. (3), the Schottky barrier was estimated to be 0.56 eV. It should be noted that the estimated Schottky barrier height was different from that based on the Mott-Schottky model and on a result of the spectroscopic method because the work function of the Ni was measured to be 5.15 ± 0.02 eV in this study. This difference is attributable to the existence of an interfacial dipole that leads to a vacuum-level shift as reported in various metal/organic systems.¹⁴ The vacuum-level shift (Δ) caused by the interfacial dipole in this study was determined to be 0.66 eV.

Next, the series resistance (R_s) in the rubrene is briefly discussed. The R_s can be regarded as the sum of the contact resistance and the resistance of the rubrene itself. The temperature dependence of R_s provides us with useful information for investigating the characteristics of R_s . If the temperature dependence of the resistance is semiconducting, the current increases with increasing temperature upon thermal excitation as

$$R_s \propto \exp \left(\frac{E_a}{kT} \right), \quad (4)$$

where E_a is the activation energy. An organic molecule without impurities is an intrinsic semiconductor. Therefore, if the rubrene single crystal possesses no impurity state, E_a is coincident with the bandgap (~ 2 eV). However, if the rubrene single crystal includes impurities, the location of the trap level can be investigated. Figure 2(c) shows the temperature dependence of R_s , where the semiconducting behavior of the R_s can be seen. E_a was calculated to be 0.18 eV, which indicates that the deep traps exist in the rubrene single crystal device. Deep traps in rubrene single-crystal OFETs have been previously reported in one study,¹⁵ where they were located within ca. 0.1 eV from the HOMO level. Our study likely indicates the existence of deeper trap levels, which has not been previously reported. Figure 3 displays the energy band diagram of the Ni/rubrene single-crystal Schottky junction based on the physical parameters obtained in this study, where the importance of the vacuum level shift and the

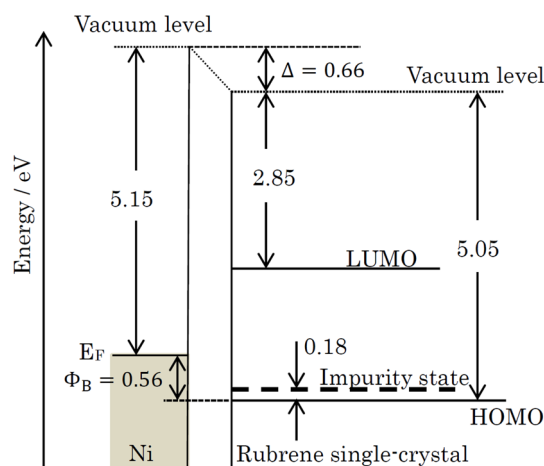


FIG. 3. (Color online) Energy band diagram of the Ni/rubrene single-crystal junction obtained in this study.

interfacial electric double layer are highlighted. From a spintronics point of view, the Schottky barrier of 0.56 eV between Ni and the rubrene single crystal seems too large for efficient spin injection. Hence, carrier doping in rubrene in order to suppress the formation of very large barriers, for example, is needed for the fabrication of spin valve devices. The finding in this study teaches us that electrical investigations of Schottky barriers at the ferromagnet/organic-SC interface are significant for realizing conclusive electrical spin injection. Although, the previous spectroscopic approaches have been introduced in many organic spin devices for clarifying the band structures, our finding shows that the electrical investigations are also significant for electric spin transport in the organic spin devices because the existence of the Schottky barrier clarified in this study has not been observed by spectroscopic methods. It is also suggested from our study that functionalization and/or carrier doping to organic SCs for obtaining the thinner and lower barriers are potential, as conducted in inorganic semiconductor spin devices.¹⁶

In conclusion, the interface electronic band structure between Ni and rubrene single crystal was quantitatively studied using an electrical method, and the band diagram of the interface between Ni and rubrene single crystal was obtained. The Schottky barrier height and vacuum-level shift were estimated to be 0.56 eV and 0.66 eV, respectively. It was also found that deep level traps in the rubrene single crystal device were located 0.18 eV above the highest occupied molecular orbital level.

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